

CORROSION PROTECTION BY
CALCITE-TYPE COATINGS

OCTOBER, 1989

Prepared by:

OCEAN CITY RESEARCH CORPORATION
Tennessee Avenue & Beach Thorofare
Ocean City, New Jersey

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE OCT 1989		2. REPORT TYPE N/A		3. DATES COVERED -	
4. TITLE AND SUBTITLE Corrosion Protection by Calcite-Type Coatings				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Surface Warfare Center CD Code 2230 - Design Integration Tools Bldg 192 Room 128 9500 MacArthur Blvd Bethesda, MD 20817-5700				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 41	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

DISCLAIMER

These reports were prepared as an account of government-sponsored work. Neither the United States, nor the Maritime Administration, nor any person acting on behalf of the Maritime Administration, (A) makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness or usefulness of the information contained in this report/manual, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or (B) assumes any liabilities with respect to the use of or for damages resulting from the use of any information, apparatus, method, or process disclosed in the report. As used in the above, "Persons acting on behalf of the Maritime Administration" includes any employee, contractor, or subcontractor to the contractor of the Maritime Administration to the extent that such employee, contractor, or subcontractor to the contractor prepares, handles, or distributes, or provides access to any information pursuant to his employment or contract or subcontract to the contractor with the Maritime Administration. ANY POSSIBLE IMPLIED WARRANTIES OF MERCHANTABILITY AND/OR FITNESS FOR PURPOSE ARE SPECIFICALLY DISCLAIMED.

FORWARD

The Maritime Administration under its National Shipbuilding Research Program sponsored the subject study. National Steel and Shipbuilding Company (NASSCO) administered the program for the Maritime Administration with Mr. Jim Ruecker of NASSCO acting as Technical Administrator. All of the experimental work described in the subject report was conducted at the Ocean City Research Corporation laboratory in Ocean City, New Jersey under the direction of Mr. George A. Gehring, Jr.

The subject study continued an investigation of the feasibility of applying calcite-type coatings to segregated seawater ballast tanks. If perfected, a calcite coating approach could substantially reduce the cost of corrosion control of segregated, seawater ballast tanks. The overall objective of the National Shipbuilding Research Program is to reduce shipbuilding-related costs in U.S. Shipyards.

EXECUTIVE SUMMARY

The shipbuilding industry has directed much effort toward ways of limiting escalating coating costs. Of special concern with respect to increasing coating costs are segregated seawater ballast tanks. The use of a calcite-type coating instead of a traditional organic-type maintenance coating represents a possible alternative approach for controlling corrosion in the segregated tanks with a substantial savings in cost. As a result, National Steel and Shipbuilding Company acting on behalf of the Maritime Administration under the National Shipbuilding Research Program authorized the Ocean City Research Corporation to undertake a laboratory study which continued previous investigations of the feasibility of applying calcite-type coatings to segregated ballast tanks. The testing was intended to demonstrate and quantify the long-term corrosion protection afforded by the calcite coatings.

The laboratory tests demonstrated that well developed calcite films can reduce the corrosion rate of steel in a seawater ballast tank. Furthermore, calcite films can reduce the cathodic protection current demand required for corrosion control by a factor of five. However, the testing also showed that calcite films will deteriorate with time upon continued exposure to seawater. Thus, such films would have to be periodically reformed given the contemplated approach.

The major impediment associated with the implementation of calcite coating technology in a segregated ballast tank is the ability to form a "good, well-developed" coating given the application constraints imposed by the typical tank configuration. At this point, there appears no practical way to overcome this impediment.

Evaluation of calcite films and calcareous deposits over inorganic zinc preconstruction primers showed that good corrosion protection could be provided to steel substrates with minimal cathodic protection current (approximately 2% of that required for uncoated steel). The test results encourage further investigation of the protection afforded by such films over zinc preconstruction primers.

TABLE OF CONTENTS

<u>Section</u>	Page
INTRODUCTION	1
CONCLUSIONS	3
RECOMMENDATIONS	4
EXPERIMENTAL APPROACH	5
RESULTS AND DISCUSSION.. . . .	9
REFERENCES	13
Table 1 -SUMMARIZED TEST MATRIX.	14
Table 2 - SUMMARY OF PANEL EXPOSURE TESTS	15
Table 3 - SUMMARY OF CURRENT VS. TIME REGRESSION ANALYSIS	16
Figure 1 - Test Panel After Pretreatment in Stirred Calcite Solution (50 Days); Prior To Seawater Ballast Cycle	17
Figure 2 - Test Panel After Pretreatment in Static Calcite Solution (50 Days) ; Prior to Seawater Ballast Cycle	17
Figure 3 - Typical Test Panel Appearance After Extended Exposure in Seawater Ballast Cycle with Cathodic Protection	18
Figure 4 - Typical Test Panel Appearance After Extended Exposure in Seawater Ballast Cycle Without Cathodic Protection	18
Figure 5 - Summary of Panel Test Results	19
Figure 6 - Typical Appearance of Steel Tank with Calcareous Coating from Seawater (Stirred Solution, 40 Days); Prior to Seawater Ballast Cycle	20
Figure 7 - Typical Appearance of Steel Tank Coated with Calcite (Stirred Solution, 40 Days) ; Prior to Seawater Ballast Cycle	21
Figure 8 - Typical Appearance of Steel Tank Coated with Calcite (Water Circulation, 40 Days) ; Prior to Seawater Ballast Cycle	22

TABLE OF CONTENTS (cont'd)

<u>Sect ion</u>	<u>Page</u>
Figure 9 - Typical Appearance of Tank Coated with Calcite (Air Agitation, 80 Days) ; Prior to Seawater Ballast Cycle	23
Figure 10 - Appearance of Steel Tank Primed with Inorganic Zinc and Coated with Calcareous Deposit (Static, 40 Days) ; Prior to Seawater Ballast Cycle	24
Figure 11 - Appearance of Steel Tank with Inorganic Zinc and Coated with Calcite (Static, 40 Days) ; Prior to Seawater Ballast Cycle	24
Figure 12 - Coating Resistance vs. Time, Control	25
Figure 13 - Coating Resistance vs. Time, Stirred Calcite	26
Figure 14 - Coating Resistance vs. Time, Recirculated Calcite	27
Figure 15 - Coating Resistance vs. Time, Air Agitated Calcite	28
Figure 16 - Coating Resistance Vs. Time, Calcareous Deposits over Zinc	29
Figure 17 - Coating Resistance vs. Time, Calcite over Zinc	30
Figure 18 - Steel Tank Originally Coated with Calcareous Deposit After 100-Day Seawater Ballast Cycle	31
Figure 19 - Steel Tank Originally Coated with Calcite Coating (Stirred Solution, 40 Days) After 100-Day Seawater Ballast Cycle	31
Figure 20 - Steel Tank Originally Coated With Calcite Coating (Water Circulation, 40 Days) After 195-Day Seawater Ballast Cycle	32
Figure 21 - Steel Tank Originally Coated with Calcite Coating (Air Agitation, 80-Days) After 155-Day Seawater Ballast Cycle	32

TABLE OF CONTENTS (cent'd)

<u>Section</u>	<u>Page</u>
Figure 22 - Steel Tank Originally Primed with Inorganic Zinc and Coated with Calcareous Deposit (Static, 40 Days) After 150-Day Seawater Ballast Cycle	33
Figure 23 - Steel Tank Originally Primed with Inorganic Zinc and Coated with Calcite (Static, 40 Days) after 150-Day Seawater Ballast Cycle	33
Figure 24 - Current Flow vs. Time for Ballast Tanks . . .	34

INTRODUCTION

One factor contributing to the escalating cost of producing ships within the United States is the application of organic coatings for corrosion control. An area of major concern regarding coating costs are segregated seawater ballast tanks. These ballast tanks are usually narrow, confined spaces with few access points. The costs of the abrasive blasting, coatings, and labor needed to coat these tanks has risen dramatically over the past 20 years. Therefore, in 1980, the Ocean City Research Corporation, under the sponsorship of the Maritime Administration, began to explore the possible use of a calcite-type coating system.

Since the early 1960's, calcite coatings have been used in the water works industry for corrosion control of cast iron water mains. The technology involved in producing a calcite coating in a water main was discussed by McCauley in 1958. (1, 2, 3) Briefly, calcite (calcium carbonate, CaCO_3) is formed on the interior surfaces of a water main by flowing a saturated calcium carbonate solution through the main. The calcite precipitates on the iron surface forming a protective coating.

It was originally envisioned that the waterworks industry technology could be transferred to the shipbuilding industry. The calcite coating could be formed by filling the tanks with a saturated solution of calcium carbonate. The solution would be prepared pierside by combining the appropriate chemicals with a water source (e.g. fire main). After a calcite-type coating was deposited, corrosion control would be maintained with sacrificial anodes as is the case when a conventional coating is used. Like a conventional coating, the calcite coating was expected to reduce the exposed area of steel, thereby minimizing the number of required anodes. It was also expected that the calcite film would be reinforced by calcareous deposit formation. Calcareous deposits (primarily magnesium hydroxide and calcium carbonate) form when steel is cathodically protected in seawater.

The anticipated advantages associated with the calcite coating approach were:

1. Significant reduction in both labor and material costs for tank surface preparation.
2. Significant reduction in the cost of coating raw materials.
3. Reduction in the cost of coating application.
4. Reduction in the cost of coating maintenance and repair.
5. Compatibility with safety and environmental regulations.

Two previous MARAD-sponsored studies have investigated the feasibility of using calcite-type coatings for corrosion control in segregated seawater ballast tanks. (4, 5) The first study attempted to duplicate the lining process used in the waterworks industry. It was found that tenacious calcite coatings could be deposited from supersaturated solutions as long as there was adequate solution flow/turbulence. Relatively thick (40 mils) coatings were deposited within 24 hours. Without agitation, however, calcite coating deposition was negligible.

A second study investigated modifications of the coating process that might overcome the need for agitated flow/turbulence to form good quality coatings. In a ballast tank, attainment of the necessary level of agitation is difficult to achieve in a practical fashion. The most promising modifications were to the solution chemistry and the use of cathodic protection to stimulate coating precipitation. Cathodic protection of steel in a calcite solution promotes calcite deposition through the same mechanism as calcareous deposits form from seawater, creation of a locally high pH at the steel surface. The application of these techniques was found to lower the velocity threshold required for coating deposition. Coatings deposited using these techniques were thin (5 mils), yet they had a high electrical resistivity. Thus they tended to reduce the amount of cathodic protection required to protect the steel substrate. The calcite coatings (calcium carbonate) also proved superior to calcareous deposits (magnesium hydroxide/calcium carbonate) for minimizing the cathodic protection current requirements.

The subject program was based on the work conducted in the two earlier studies. The primary objectives of the study were:

- o To document the actual level of corrosion protection afforded by the calcite coatings to steel in a simulated ballast tank environment (i.e., wet-dry cycling).
- o To determine the extent to which a calcite-type coating deposited in a ballast tank-type configuration would perform over extended periods.

CONCLUSIONS

1. Well-developed calcite coatings can reduce the corrosion rate of steel exposed cyclically to seawater ballasting. These coatings offer significantly more protection than the calcareous deposits formed on cathodically protected steel in seawater.
2. In conjunction with cathodic protection, well-developed calcite coatings can essentially eliminate corrosion that would otherwise be expected during the surface-drying time of a ballast cycle.
3. Based on a 150-day test conducted in the subject study, calcite films may be expected to reduce cathodic protection current demand required for complete corrosion protection by a factor of 5.
4. The protective properties of a calcite coating will deteriorate with time. At exposure times beyond those investigated (1/2 year), the benefit of calcite films can be expected to decrease.
5. Obtaining a "well developed" calcite film on a steel ballast tank surface remains problematic. The subject program continued to demonstrate the importance of solution agitation and coating time for adequate calcite film development. The long coating periods (80 days) and agitation requirements do not appear practical for shipboard applications.
6. Either calcareous or calcite-type films developed over inorganic zinc preconstruction primers greatly reduce the cathodic protection current required for corrosion protection of steel in seawater. The required current is about 2.0-2.5% of that required for bare steel. This reduction in current demand appears related primarily to the steel polarization attributable to the zinc within the primers and the extent of steel surface covered (isolated) from the seawater electrolyte by the primer.

RECOMMENDATIONS

1. Because there does not appear to be a practical way to develop high quality, consistent calcite films given the configuration constraints of a ballast tank, it does not appear worthwhile to pursue additional research in this area, despite the corrosion protection and reduction in cathodic protection current demand demonstrated by the calcite films.
2. Investigations should continue regarding the effectiveness of inorganic zinc preconstruction primers in conjunction with zinc anodes for corrosion control in ballast tanks. This effort should identify the effect of key variables such as type of inorganic zinc, zinc loading in the dry film, and primer thickness. The investigations should focus primarily on inorganic zinc primer/zinc anode/seawater combinations. The additional 20% reduction in current demand provided by a calcite film vs. a calcareous deposit probably does not justify the cost of a calcite pretreatment.

EXPERIMENTAL APPROACH

Tank Tests

Table 1 summarizes the test matrix. In total, six different coating situations were evaluated. The tests were conducted in square, steel tanks designed to resemble the flat sides and corners of a seawater ballast tank. The steel tank dimensions used in the subject study were nominally 12 inches square. The tanks were fabricated from welded 1010 steel. During all experiments, a liquid level of 11 inches was maintained in the tanks. A centrally located zinc anode (5 inches long by 0.75-inch diameter) was suspended from a PVC tank cover.

In each experiment, a calcite-type coating was developed on the tank surface over a 40-day time period.* Generally, tank surface preparation consisted of a light sweep blast to remove any mill-scale followed by solvent cleaning to remove any grease or residue. In two selected tests, the blasted steel substrate was coated with 0.5 - 1.0 mil of an inorganic zinc preconstruction primer (Hempel Marine Galvosil 1570). This preparation was selected based on the results of studies which have suggested that calcareous deposits (natural carbonate-type films deposited on steel under cathodic protection in seawater) over preconstruction primers provide good corrosion control in ballast tanks. (6)

During the pretreatment phase, coatings were developed from supersaturated calcite solution. As an experimental benchmark, calcareous deposit-type coatings were also developed from seawater. In some tests, coating development was enhanced by solution agitation. For each test condition, the coatings were developed while the steel substrate was under cathodic protection from a sacrificial zinc anode (-1.05 volt vs. SCE).

Following the development of a calcite coating or calcareous deposit, the tanks were subjected to a simulated ballast exposure. The simulated ballast cycle consisted of five days filled with static natural seawater and two days dry. The dry-period was sufficient to completely dry the coating. The tank remained under cathodic protection from a zinc anode during the ballast cycle.

During the pretreatment coating phase and the simulated ballast phase, the electrical resistance of each coating was determined. The electrical resistance provided an indication of the extent of the steel surface effectively covered.

* In tank #4, the coating was formed over an 80-day period, 40 days with agitation and 40 days with agitation plus heat.

At the conclusion of the simulated ballast exposure (100 to 195 days), selected tanks were subjected to polarization tests. For this testing, the tanks were filled with natural seawater and coupled to a zinc anode centrally mounted in the tanks. The current flow to the tank and the electrochemical potential of the steel tank were constantly monitored versus time. The data obtained were used to predict the required level of cathodic protection on a ballast tank with a similar type coating.

Panel Tests

In addition to the tank tests, a number of tests were conducted on small test panels. The test panels permitted mass-loss determinations at the end of testing. Steel corrosion rates could be determined for various coating methods, providing a quantitative measure of the effectiveness of the calcite coatings in the absence of cathodic protection. The test panels were cold-rolled 1020 steel, measuring 3 inches by 5 inches by 0.032 inch thick.

For the pretreatment coating phase of these tests, the test panels were suspended with cathodic protection (zinc anode) in the center of steel tanks containing either static or stirred calcite solutions. The panels remained in these tanks for either four hours, 1 day, 7 days or 50 days. Following this pretreatment period, the panels were placed into a large plastic tank where they were subjected to a five-day wet/two-day dry natural seawater ballast cycle. Test panels without a calcite film were included in the plastic ballast tank. The panels were exposed in the ballast cycle with and without cathodic protection (from a zinc anode). Table 2 summarizes the test panel conditions.

Some of the test panels were exposed in the steel tanks. The panels were placed midway between the steel walls and the zinc anode and were parallel to the walls. Two insulated wires were connected to each test panel. One was used to couple the panel to the zinc anode and the other was used for electrical measurements.

Agitation Methods

Three agitation methods were evaluated: mechanical stirring, air agitation, and water circulation. The mechanical stirrer was a one-inch diameter, three-bladed propeller attached to a variable speed synchronous motor. The propeller was located near the center of each tank at a depth of six inches. The motor was attached to the PVC cover plate. During agitation, the motor was rotated at its maximum speed of 200 rpm.

The air agitation equipment consisted of a small air compressor and a "squarell assembly of 1-inch diameter PVC pipe. This PVC plenum carried compressed air to the bottom of the tank.

The "square" portion of the assembly contained 120 evenly spaced holes from which air would escape. The compressed air from these holes agitated the solution.

The water circulation tank included a 1/2-inch diameter tube with a 90-degree elbow immersed in the solution. The outlet from the elbow was located 1/2 inch from the tank wall. The water flow rate from the tube was maintained at 10 gpm. The inlet side of the pump was connected to a segment of PVC pipe on the other side of the tank.

The effect of air agitation in conjunction with heating was also evaluated. For this test, the tank was warmed by a heating tape wrapped around the outside tank walls.

Solution Chemistry

All of the calcite protective films were formed from a similar solution chemistry. The solution consisted of 10,000 ppm calcium (as calcium chloride) and 150 ppm bicarbonate (as sodium bicarbonate) mixed in tap water. The pH of the solution was initially adjusted to 7.8 using either hydrochloric acid or sodium hydroxide as appropriate. During the calcite pretreatment phase, the calcite solution was changed on a weekly basis.

The chemistry of the calcite solution and the natural seawater was periodically monitored. This included the calcium content, carbonate content, solution pH, dissolved oxygen level, and temperature of the calcite or seawater. The levels of calcium, carbonate, and dissolved oxygen in the solution were determined using Chemetrics Corporation's Titrets. The Titrets contained premeasured quantities of indicator reagents. The color intensity of the titrate after extracting a sample was measured with a spectrophotometer to determine the concentration of interest. A Chemcadet pH meter, calibrated using pH 7.00 and pH 10.00 buffers, was used to measure the pH of the solutions.

Data Collection

The resistance of the calcite coating or calcareous deposit was determined periodically using a four-point electrical measurement technique. In this procedure, the voltage change between the tank wall and a saturated calomel reference electrode was monitored while the cathodic protection current from the zinc anode was interrupted. The interruption of cathodic protection current caused an instantaneous shift in the potential measured at the tank wall. This voltage shift is equivalent to the current flowing before interruption times the resistance of the coating. (This assumes that the entire voltage drop is across the calcite coating.) The coating resistance was determined as the instantaneous voltage shift divided by the current flow. For these measurements, the voltage shift was measured on an Al-

len 715 X-Y plotter. The X-axis was placed into a time-base mode and the voltage change recorded on the Y-axis. The voltage change could be recorded as a function of time at the moment of current interruption. The current measurements were made on an Aardvark PEC-1 zero-resistance ammeter.

The polarization measurements at the end of the test period were made using the Aardvark PEC-1 ammeter and a Aardvark High Impedance Electrometer. The ammeter was in series between the zinc anode and the steel tank wall. The electrometer recorded the voltage of the tank wall versus a saturated calomel electrode. The output from each instrument was recorded by individual Cole Parmer Instrument Company strip chart recorders.

Mass-loss data was obtained on the test panels using the guidelines outlined in ASTM G-1. Before exposure, each panel was weighed to the nearest 0.1 gram on a Torbal balance. After exposure, the panels were descaled in a solution of concentrated hydrochloric acid containing 50 g/l of stannous chloride and 20 g/l of antimony chloride. (The acid solution dissolved any remaining calcite solution). The panels were then dried in a dessicator and reweighed. The mass-loss determined was converted to a corrosion rate in mini-inches per year (mpy).

RESULTS AND DISCUSSIONS

Panel Tests

Figures 1 and 2 show the appearance of test panels after a 50-day pretreatment in static and stirred calcite solutions. After the pretreatment, the calcite film on the panel from the stirred tank evenly coated the surface. The coating on the panel in the static tank was uneven, with a heavy crystalline deposit typically on the lower edge. These panels were representative of those which had been pretreated for the shorter durations of 1 or 7 days. The panels which had been pretreated for only 4 hours had a very light, uneven deposit.

Figures 3 and 4 show the typical appearance after the simulated seawater ballast exposure. Figure 3 shows a panel which had been under cathodic protection from a zinc anode. The surface of the panel retained a light brown, calcite film intermingled with calcareous deposits. A few pinholes or defects were visible in the coating as rust spots. This corrosion presumably occurred during the drying period of the ballast cycle while the panel was not cathodically protected. After the simulated ballast exposure tests, the appearance of all the test panels under cathodic protection was very similar. Differences were no longer apparent between test panels pretreated under static or stirred conditions. Figure 4 shows a typically corroded test panel after the seawater ballast exposure test. Virtually all the unprotected panels had a similar appearance after the exposure test regardless of the initial treatment.

Figure 5 summarizes the corrosion rate data obtained by mass loss on the test panels. The data show that extension of the calcite pretreatment time tends to lower the expected steel corrosion rate during the subsequent ballast exposure. This was true for panels exposed in the ballast phase with or without cathodic protection. The panels exposed during the ballast phase with cathodic protection have, as would be expected, a significantly lower corrosion rate than those exposed without cathodic protection. The panels exposed with cathodic protection following the 50-day stirred calcite solution pretreatment showed no measurable corrosion rate. Of the panels exposed either with or without cathodic protection during the ballast phase, three of the four calcite pretreatment times resulted in a corrosion rate reduction for the panel with the calcite film formed under stirred conditions.

Steel Tank Tests

Figures 6 through 11 show the visual appearance of the steel test tanks coated with either calcareous deposits or calcite films. The typical calcareous deposits formed from seawater (Figure 6) were a soft, white, non-tenacious product. This coat-

ing was fairly evenly distributed on the tank walls yet only partially covered the tank bottom. The coating formed from the calcite solution (Figure 7) under similar conditions were thinner in appearance and evenly covered most of the wetted tank area. The calcite film formed under the more vigorous agitation of water circulation (Figure 8) was thicker and more evenly distributed than that formed under simple stirring. The coating in tank corners was superior to that formed under the stirred condition. The coating covered all areas evenly except for the point of solution impingement on the tank wall. In this region, a thin yet tenacious calcite film appeared. The coating was darker in color to the surrounding film. The film formed over 80 days by air agitation followed by air agitation with heat was the thickest of the calcite coatings. The tank walls were coated with large calcite nodules in some places. The tank bottom was well covered with an even calcite layer -- although some areas were covered with a thin, dark coating similar to that found in the impingement zone of the tank with water circulation.

Figure 10 shows the tank with inorganic zinc primer exposed to seawater under cathodic protection. After the 40-day pretreatment phase, a white calcareous layer covered the majority of the zinc primer. Figure 11 shows a steel tank with the inorganic zinc coated with a calcite film. The calcite film exhibited its characteristic brown color and lightly covered the zinc primer. Both the calcareous deposit and the calcite film evenly covered the zinc primer.

Figures 12 through 17 present the results of the coating resistance measurements made on the steel tanks during the pretreatment phase and after the change-over to the simulated ballast exposure. The calcareous deposit in the control tank (Figure 12) exhibited little electrical resistance during the pretreatment phase or ballast phase. By contrast, the tank with the calcite film formed by stirring developed a resistance of about 25 ohm-ft² during the 40-day calcite pretreatment. Immediately upon exposure to the seawater ballast cycle, the tank wall coating resistance decreased. Within 30-days, the wall coating resistance had decreased to 2 ohm-ft² and remained at this level for the duration of the ballast cycle. By the end of the ballast exposure, the wall coating resistance was approximately 2 ohm-ft² for the tank with the calcite pretreatment vs. 0.2 ohm-ft² for the tank with the seawater pretreatment.

Figures 14 and 15 present the coating resistance plots for the calcite films formed by a circulating solution and by air agitation. Before the ballast exposure, both films achieved a resistance around 125 ohm-ft². This was approximately 5 times the resistance on the films formed in a stirred calcite solution. After changing to the ballast cycle, the coating resistance of the film formed by solution circulation decreased drastically from 120 ohm-ft² to 20 ohm-ft². The coating resistance then decreased slowly to about 15 ohm-ft² by the end of the ballast exposure. The coating resistance of the film formed by air agita-

tion also decreased, although less drastically, during the ballast phase. The final coating resistance was approximately 37 ohm-ft²

Figure 16 depicts the coating resistance behavior of the calcareous deposits over the zinc primer. Over the initial 40-day pretreatment phase, the coating resistance rose to about 15 Ohm-ftz. Upon initiation of the ballast cycle, there was no decrease in the coating resistance. During the ballast phase, the coating resistance continued to rise to 25 ohm-ft².

Figure 17 shows the electrical resistance behavior of the calcite film over the zinc primer. The coating exhibited a rapid rise in resistance to 80 ohm-ft² at the start of the ballast cycle. The resistance continued to rise after the start of the ballast cycle. After 35 days of the ballast cycle, the coating resistance had risen to 150 ohm-ft². From this point, the resistance decreased to about 100 ohm-ft² and appeared relatively stable for the remainder of the ballast cycle. The coatings (calcareous or calcite) over the inorganic zinc preconstruction primers were the only coatings to show an increase in coating resistance during the ballast cycle.

Figures 18 through 23 show the visual appearance of the test tanks following the extended seawater ballast cycles. The tank with the calcareous deposit (Figure 18) exhibited little rusting. There were areas with spalling film and light rust. The tanks with the calcite films (Figures 19 to 21) showed no heavy rusting. Rusting was evident at pinholes or coating flaws. There were no gross changes in the appearance of the films over the course of the exposure test that can be related to the significant decrease in coating resistivity observed during the ballast phase. The tanks with the zinc primers appeared in excellent condition after an extended 150-day seawater ballast cycle. No corrosion or metal loss was observed on any portion of the tank walls.

Cathodic Protection Current Demand

Figure 24 presents current demand vs. time behavior for the tank with the calcite film formed by air agitation and the tanks with the zinc primers. The air agitation calcite tank was selected because it appeared to have the best film as indicated by coating resistance. All of these tanks were polarized to an electronegative potential of -1.05 volts vs. SCE (zinc anode) by the completion of the exposure. The current vs. time behavior of each tank decreased with time. The data set for each tank was regressed as an inverse function of time to determine the probable steady-state cathodic protection current requirements. Table 3 presents the results of these regression analyses. Based on the analyses, the predicted steady state current for each case would be:

<u>Coating</u>	Current Demand	
	ma	<u>mA/ ft</u>
Air Agitated Calcite	10.6	2.12
Zinc Primer\ Calcareous Deposit	1.2	0.24
Zinc Primer\ Calcite Deposit	1.0	0.20

For a similar bare steel tank, the required cathodic protection current to polarize the tank to -1.05 volts would be 50 MA for approximately 5 ft² of exposed steel. Greater than 25 mA were required to polarize the control tank (calcareous coating) in the subject study to -0.800 volt vs. SCE.

It is interesting to note the corrosion potentials exhibited by the steel tanks with the calcite coatings and those with the zinc primers. Those with the calcite coating were about -0.6 volt vs. SCE -- the typical corrosion potential of steel in seawater. The tanks with the zinc primer exhibited potentials of about -0.95 volt, demonstrating that the zinc within the primer was catholically polarizing the steel substrate in the absence of external cathodic protection.

REFERENCES

- . R. F. McCauley, Journal AWWA, Vol. 49, October 1957, p. 1303.
2. R. F. McCauley and M. O. Abdullah, Journal AWWA, Vol. 50 November, 1958, p. 1419.
3. R. F. McCauley, Journal AWWA, Vol. 52, November, 1960, p. 1386.
4. "A Laboratory Study Investigating the Feasibility of Applying Calcite-Type Coatings to Segregated Ballast Tanks," a report authored by Ocean City Research Corporation for the Maritime Administration, August, 1981.
5. "An Investigation of Possible Ways To Enhance the Deposition of Calcite-Type Coatings," a report authored by Ocean City Research Corporation for the Maritime Administration, January, 1984.
6. "New Surface Preparation and Repair Techniques for Ballast Tanks," B. Fultz, SNAME Panel SP-3 project task 3-82-3, interim results presented in Jacksonville, FL, February, 1989.

Table 1

SUMMARIZED TEST MATRIX

<u>Test Number</u>	<u>Steel Wall Preparation</u>	<u>Coating Solution</u>	<u>Agitation Method</u>	<u>Pretreatment Coating Duration, days</u>	<u>Seawater Ballast Cycle Duration, days</u>
#1	Sweepblast	Seawater	Stirred	40	100
#2	Sweepblast	Calcite	Stirred	40	100
#3	Sweepblast	Calcite	Water Circulation	40	195
#4	Sweepblast	Calcite	Air Agitation +	40	155
			Air Agitation with Heat	40	
#5	Inorganic Zinc Pre-Const. Primer	Seawater	None	40	150
#6	Inorganic Zinc Pre Const. Primer	Calcite	None	40	150

Table 2

SUMMARY OF PANEL EXPOSURE TESTS

<u>Test Panel</u>	<u>Pretreatment Time in Calcite Coating Solution</u>	<u>Calcite Solution Stirred</u>	<u>Time in Ballast Tank. hours</u>	<u>Cathodic Protection in Ballast Tank (Zinc Anode)</u>
1	0 Hours		1246	yes
2	0 Hours		1246	no
3	0 Hours		7968	yes
4	0 Hours		7968	no
5	4 Hours	yes	1242	yes
6	4 Hours	yes	1242	no
7	4 Hours	no	1242	yes
8	4 Hours	no	1242	no
9	1 Day	yes	1219	yes
10	1 Day	yes	1219	no
11	1 Day	no	1219	yes
12	1 Day	no	1219	no
13	7 Days	yes	1079	yes
14	7 Days	yes	1079	no
15	7 Days	no	1079	yes
16	7 Days	no	1079	no
17	50 Days	yes	6888	yes
18	50 Days	yes	6888	yes
19	50 Days	yes	6888	no
20	50 Days	yes	6888	no
21	50 Days	no	6888	yes
22	50 Days	no	6888	yes
23	50 Days	no	6888	no
24	50 Days	no	6888	no

Table 3

SUMMARY OF CURRENT VS. TIME
REGRESSION ANALYSIS

Air-Agitated Calcite Coating	$\text{Current} = (44.9 \backslash \text{Hours}) + 10.6$ (m) $R = 0.94$
Inorganic Zinc Primer/Seawater	$\text{Current} = (0.24 \backslash \text{Hours}) + 1.2$ (ma) $R = 0.89$
Inorganic Zinc Primer/Calcite	$\text{Current} = (0.31 \backslash \text{Hours}) + 1.0$ (ma) $R = 0.72$

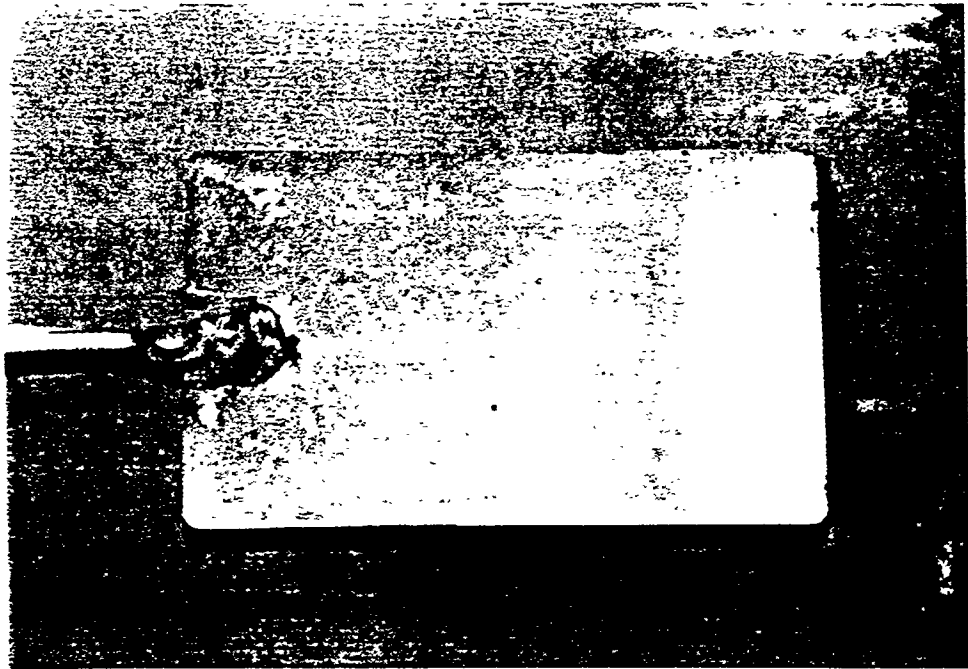


Figure 1 - Test Panel After Pretreatment in Stirred Calcite Solution (50 Days); Prior To Seawater Ballast Cycle

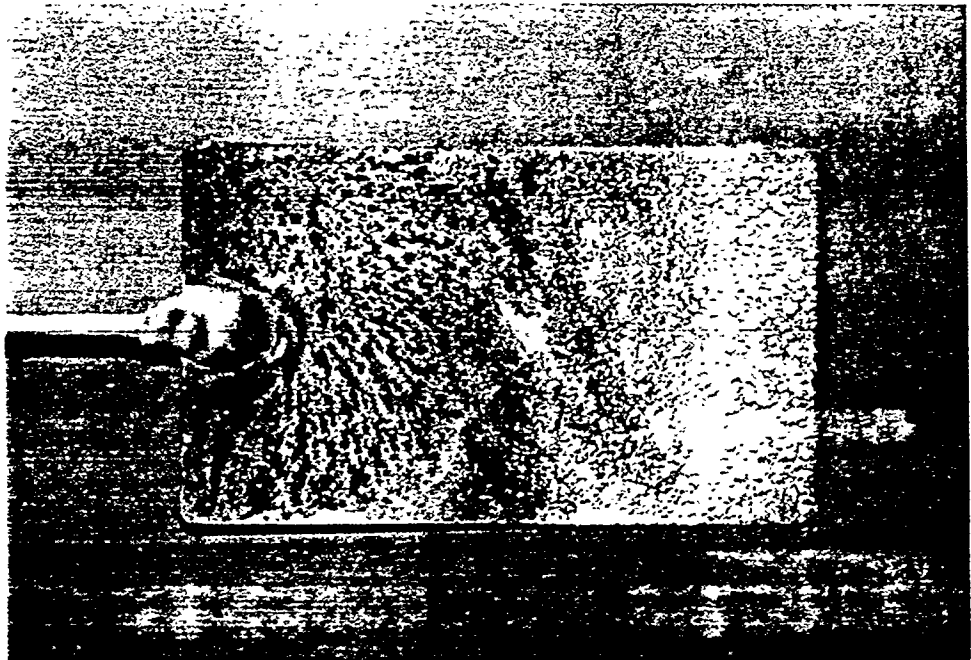


Figure 2 - Test Panel After Pretreatment in Static Calcite Solution (50 Days); Prior to Seawater Ballast Cycle

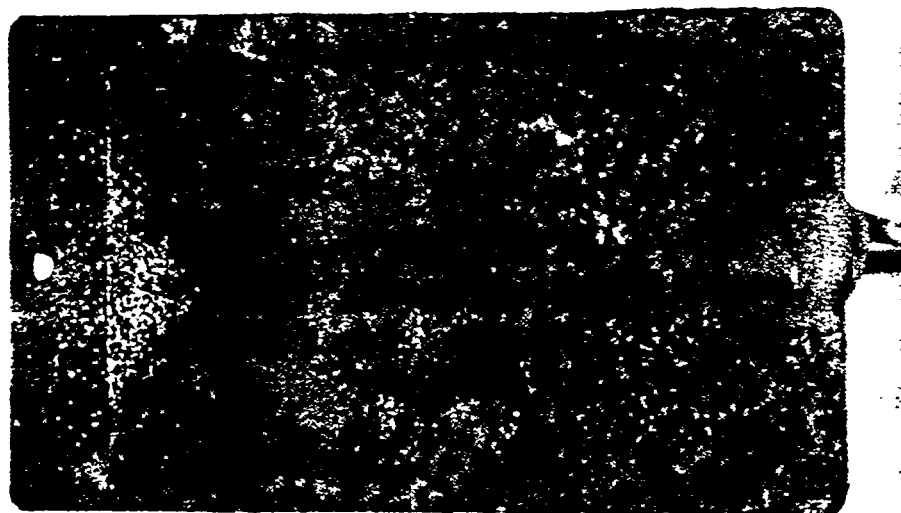


Figure 3 - Typical Test Panel Appearance After Extended Exposure in Seawater Ballast Cycle with Cathodic Protection (Note: bottom edge was epoxy coated prior to the test.)

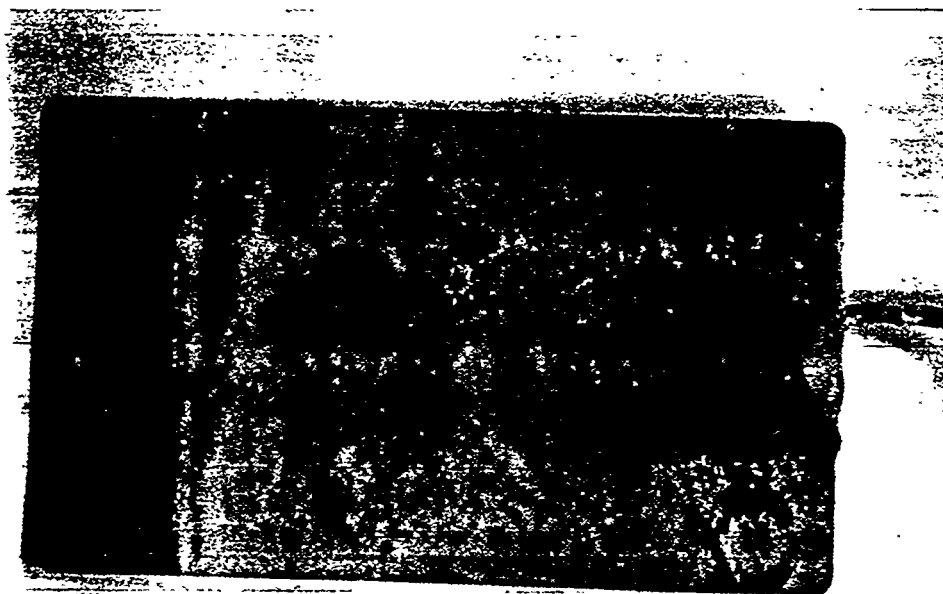
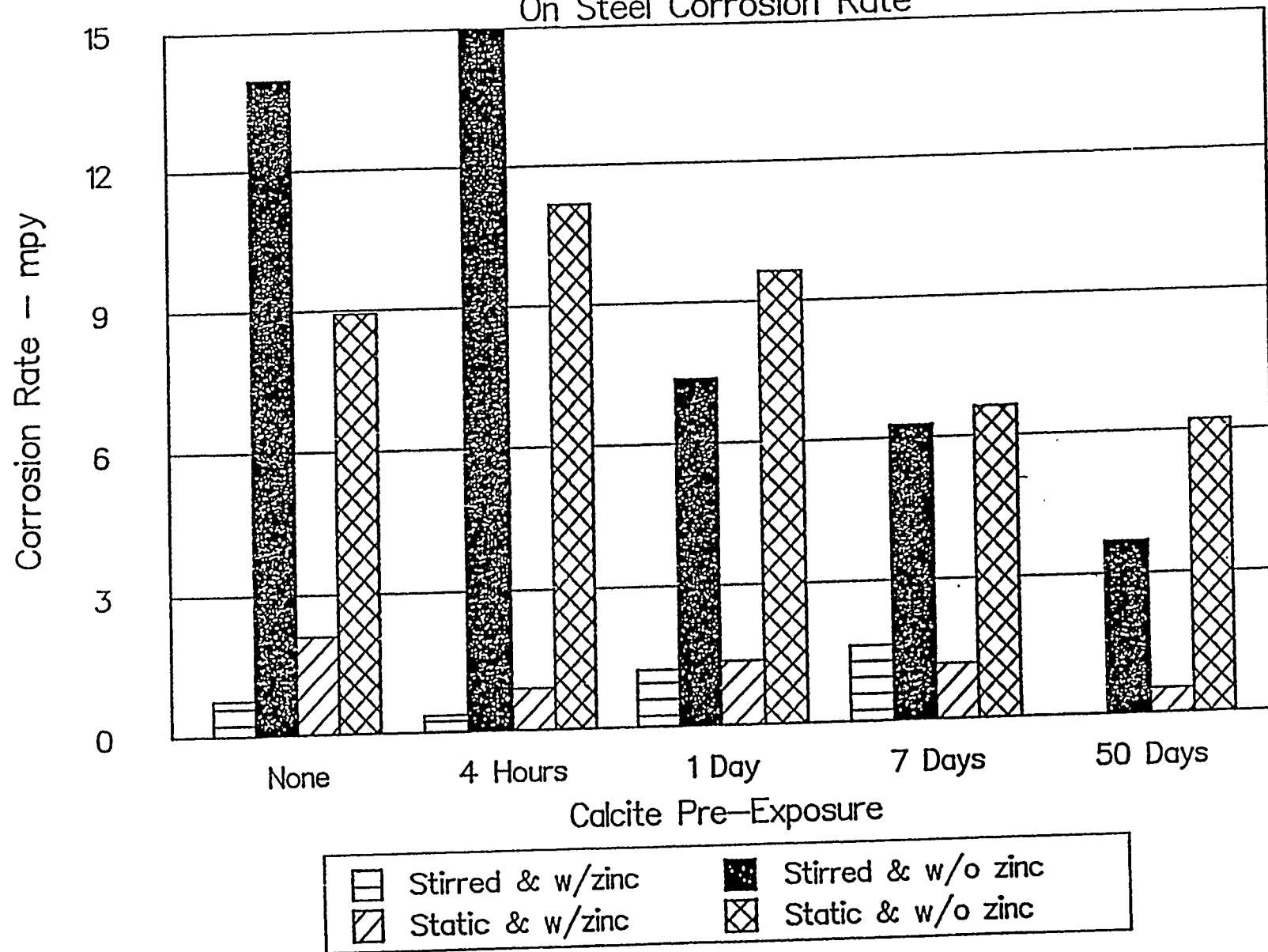


Figure 4 - Typical Test Panel Appearance After Extended Exposure in Seawater Ballast Cycle Without Cathodic Protection

Effect of Calcite Pre-Exposure On Steel Corrosion Rate



NOTE: COMMENTS REGARDING STIRRED OR STATIC CALCITE
BATH DURING PRE-EXPOSURE NOT RELEVANT TO SAMPLES
WITH '0' PRE-EXPOSURE

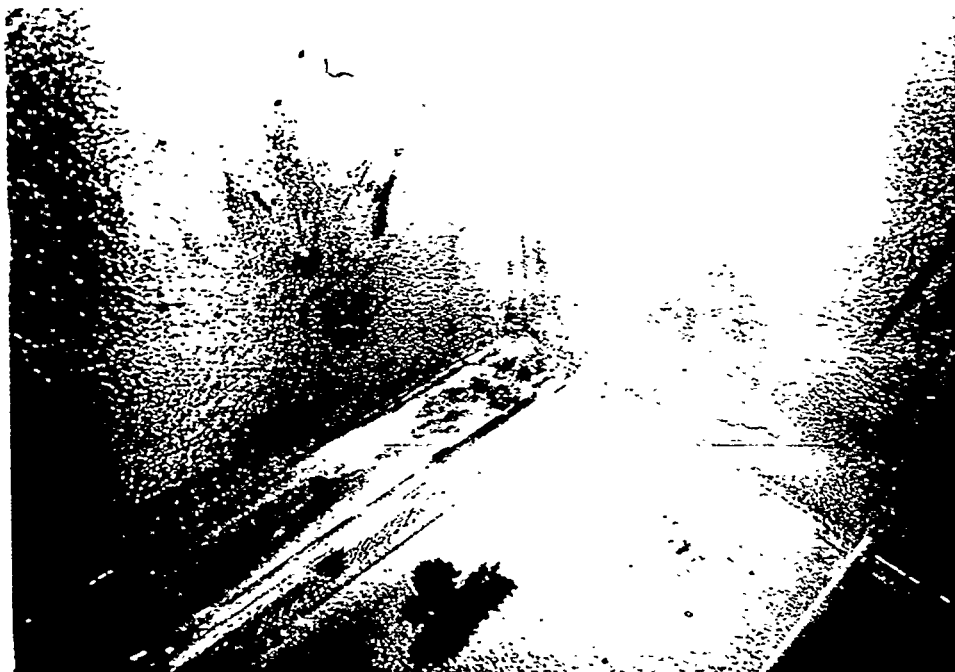
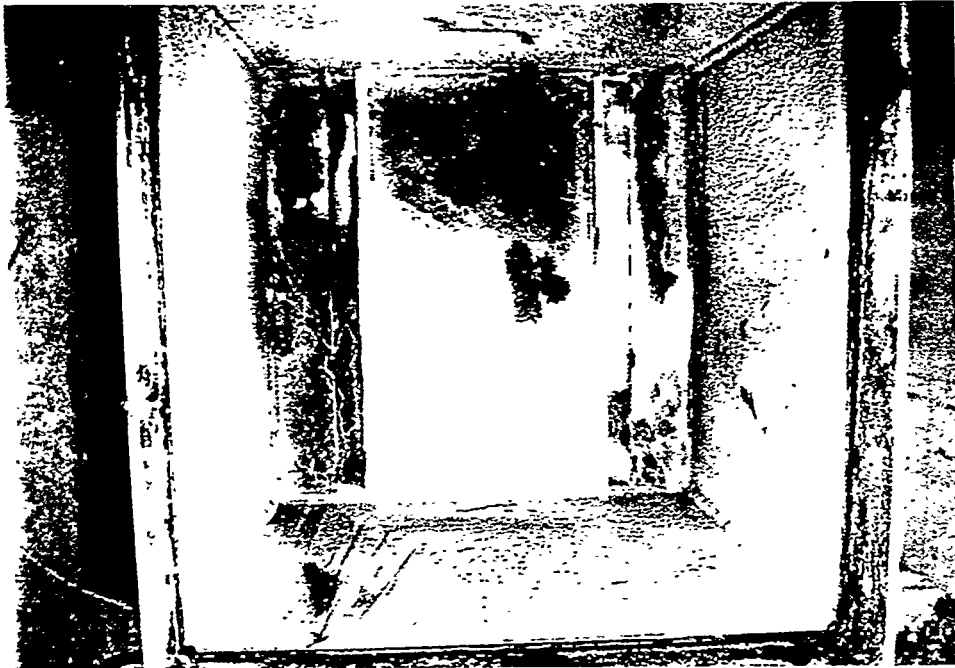


Figure 6 - Typical Appearance of Steel Tank with Calcareous Coating from Seawater (Stirred Solution, 40 Days); Prior to Seawater Ballast Cycle



Figure 7 - Typical Appearance of Steel Tank Coated with Calcite (Stirred Solution, 40 Days); Prior to Seawater Ballast Cycle

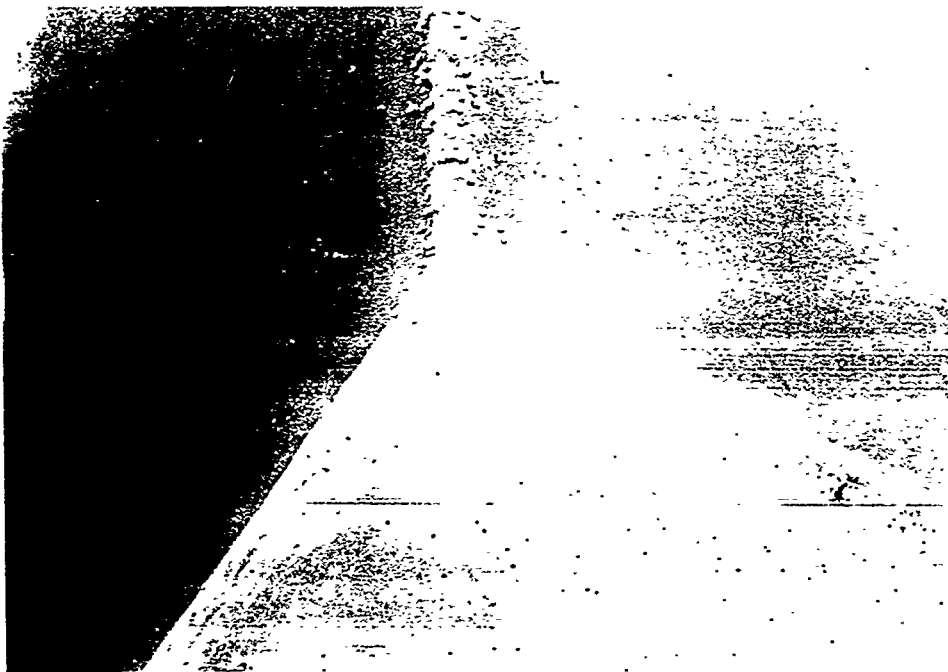
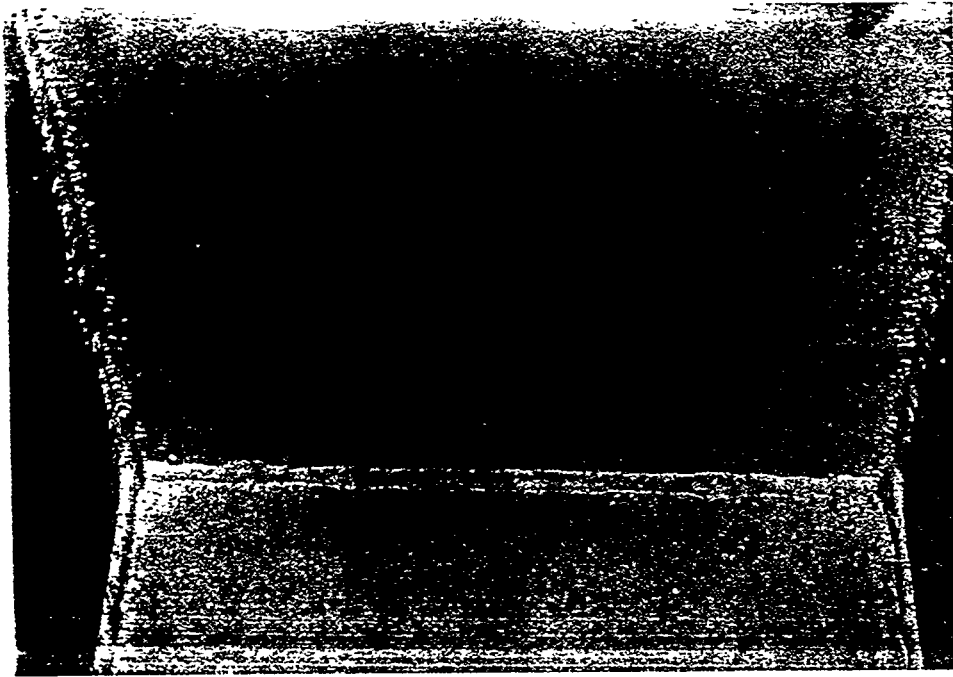


Figure 8 - Typical Appearance of Steel Tank Coated
with Calcite (Water Circulation, 40 Days);
Prior to Seawater Ballast Cycle
(Note: upper photograph shows impinge-
ment point for circulating solution.)

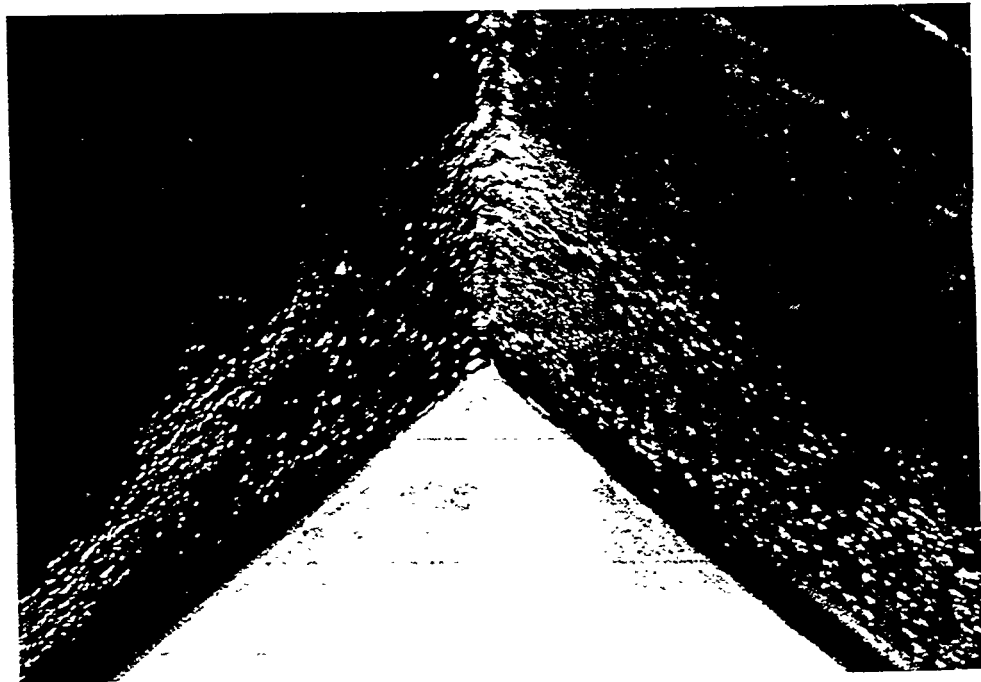
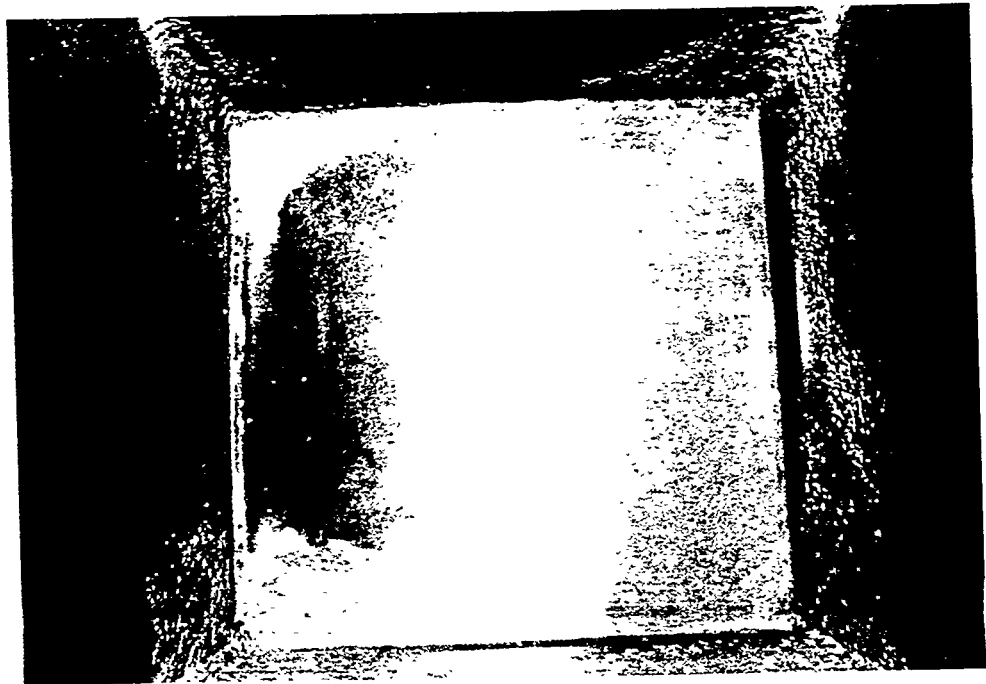


Figure 9 - Typical Appearance of Tank Coated with Calcite (Air Agitation, 80 Days); Prior to Seawater Ballast Cycle

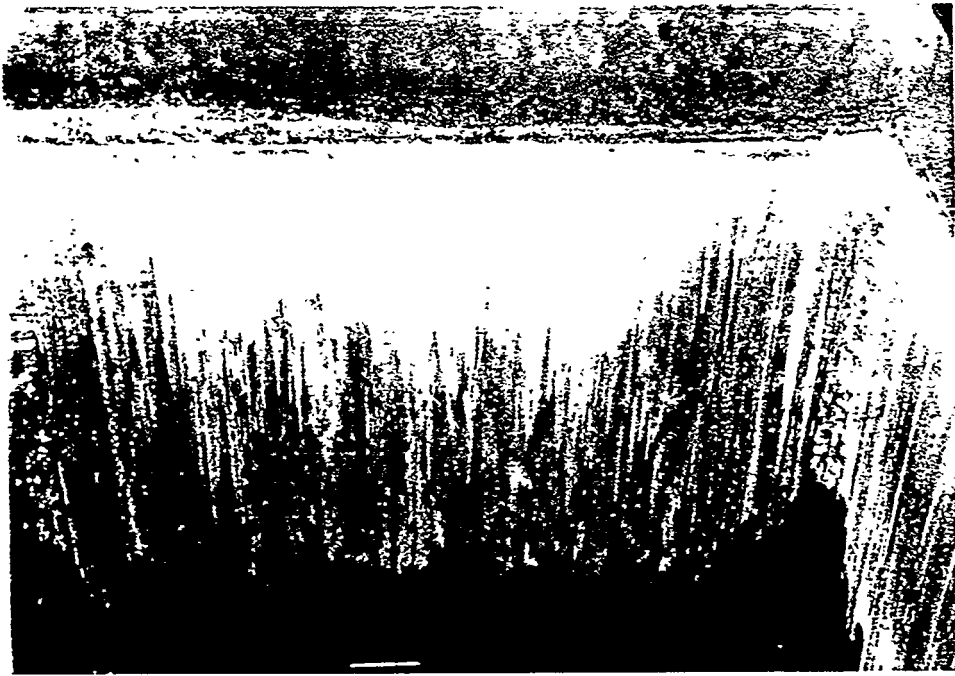


Figure 10 - Appearance of Steel Tank Primed with Inorganic Zinc and Coated with Calcareous Deposit (Static, 40 Days); Prior to Seawater Ballast Cycle. (Note: the dark bottom area is simply wet at the time of photography.)

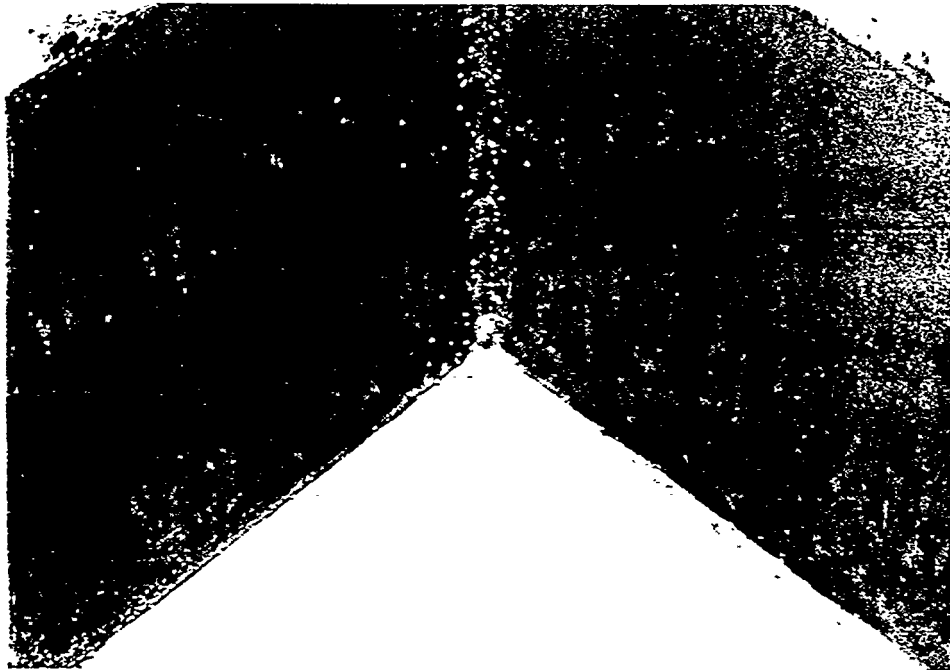


Figure 11 - Appearance of Steel Tank with Inorganic Zinc and Coated with Calcite (Static, 40 Days) ; Prior to Seawater Ballast Cycle

Calcareous Deposit Formed With Stirring (Control)

25

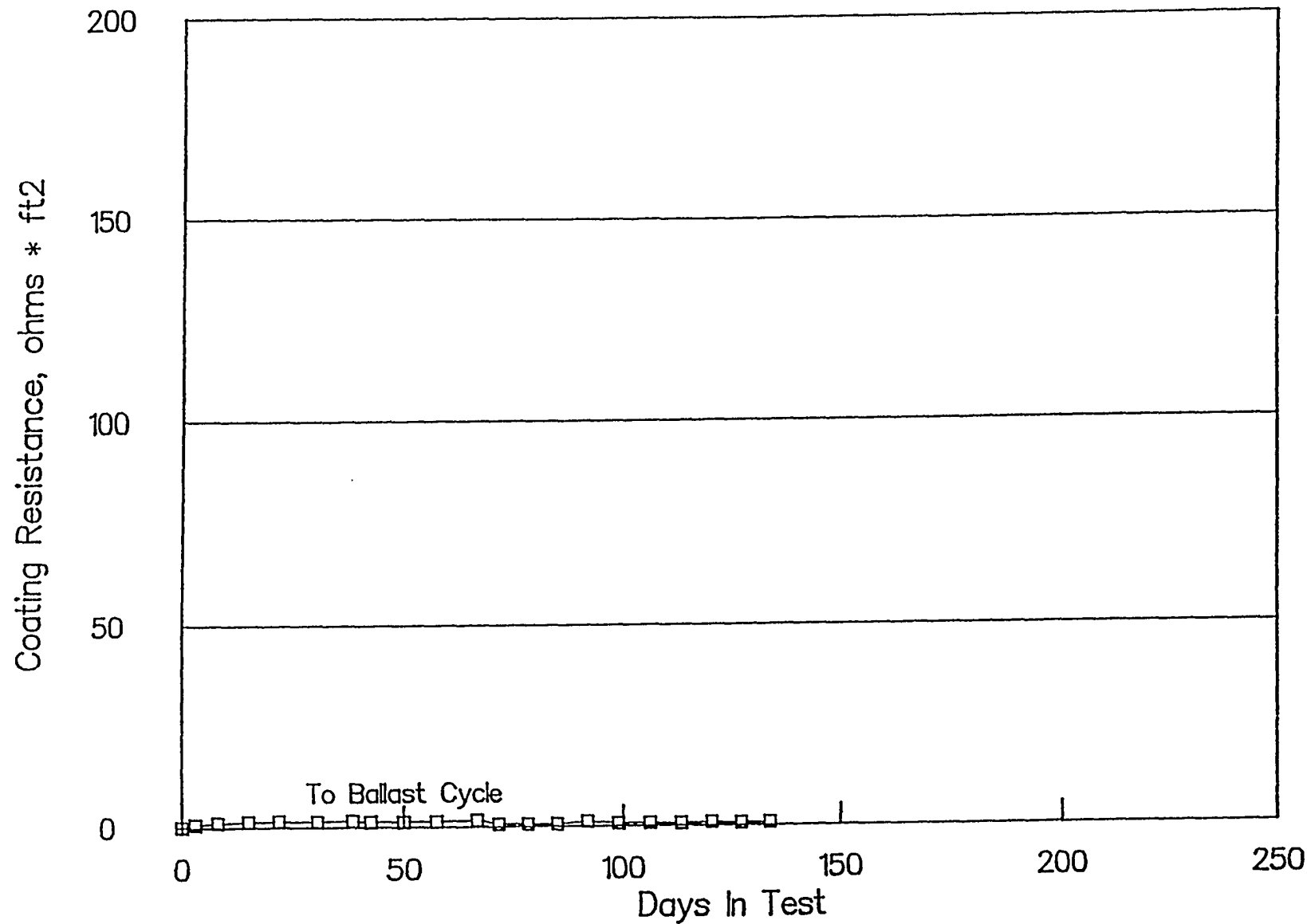


Figure 12 - Coating Resistance vs. Time, Control

Calcite Coating Formed By Stirring

26

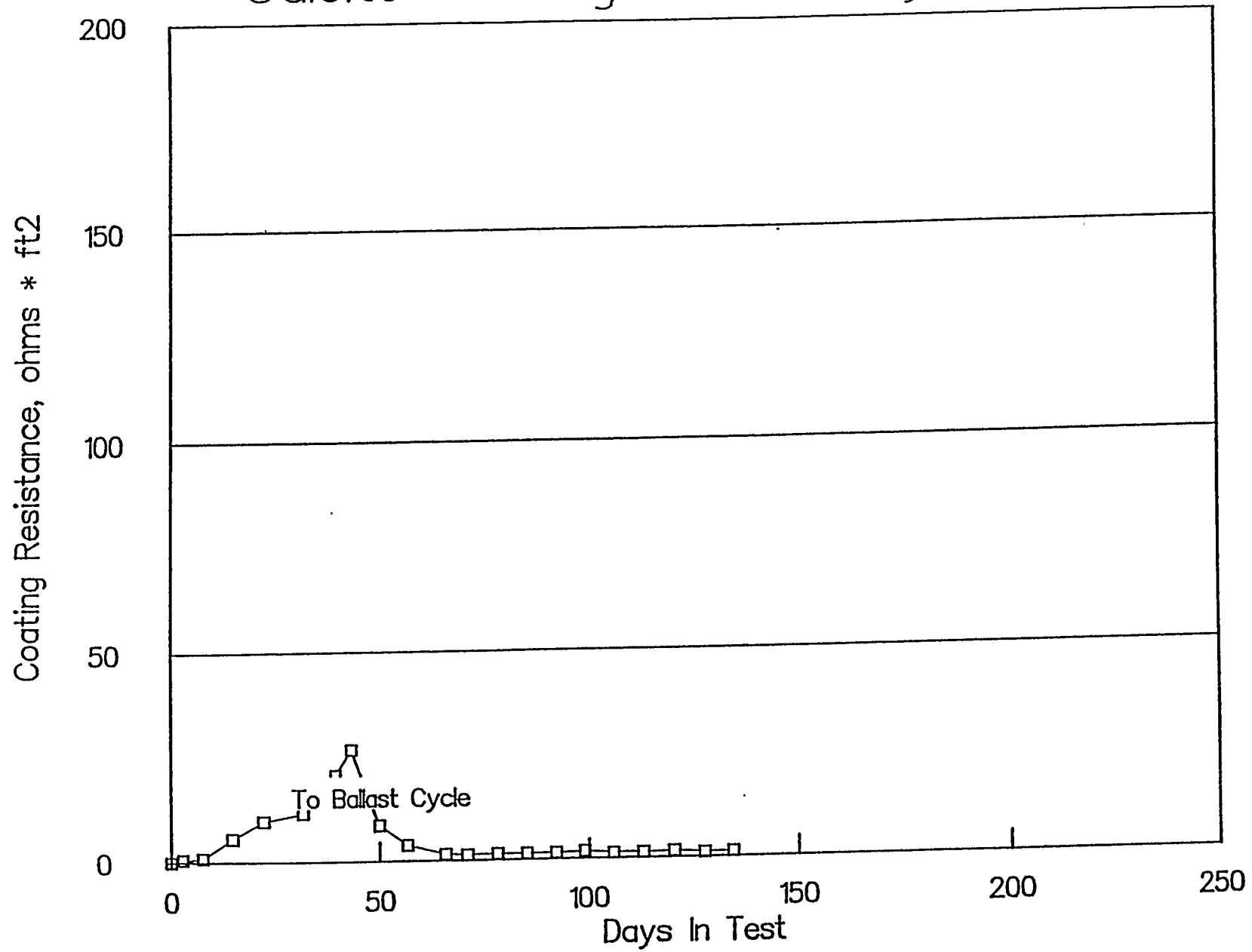


Figure 13 - Coating Resistance vs. Time, Stirred Calcite

Calcite Coating Formed With
Recirculating Solution

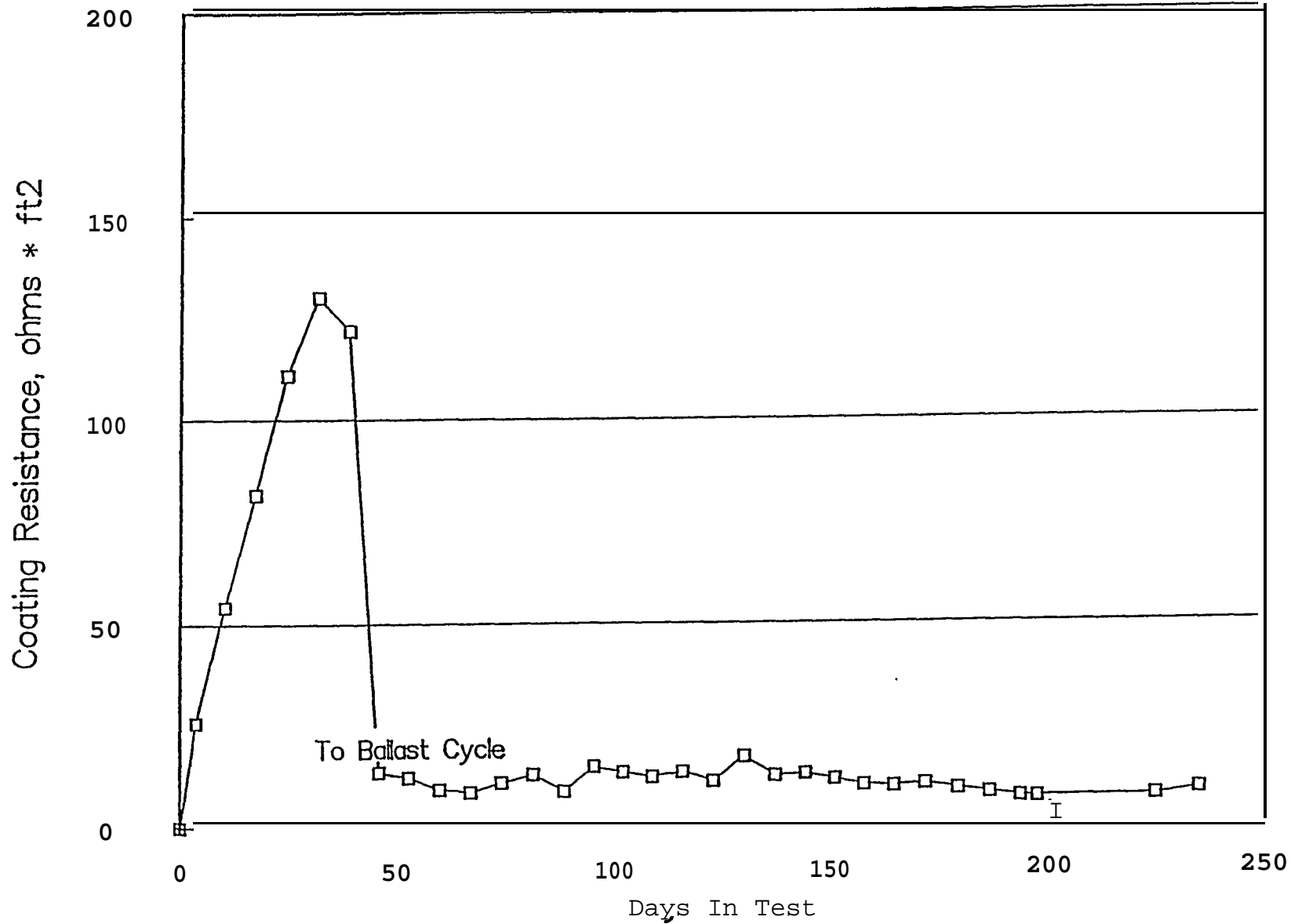


Figure 14 - Coating Resistance vs. Time, Recirculated Calcite

Calcite Coating Formed With Air Agitation

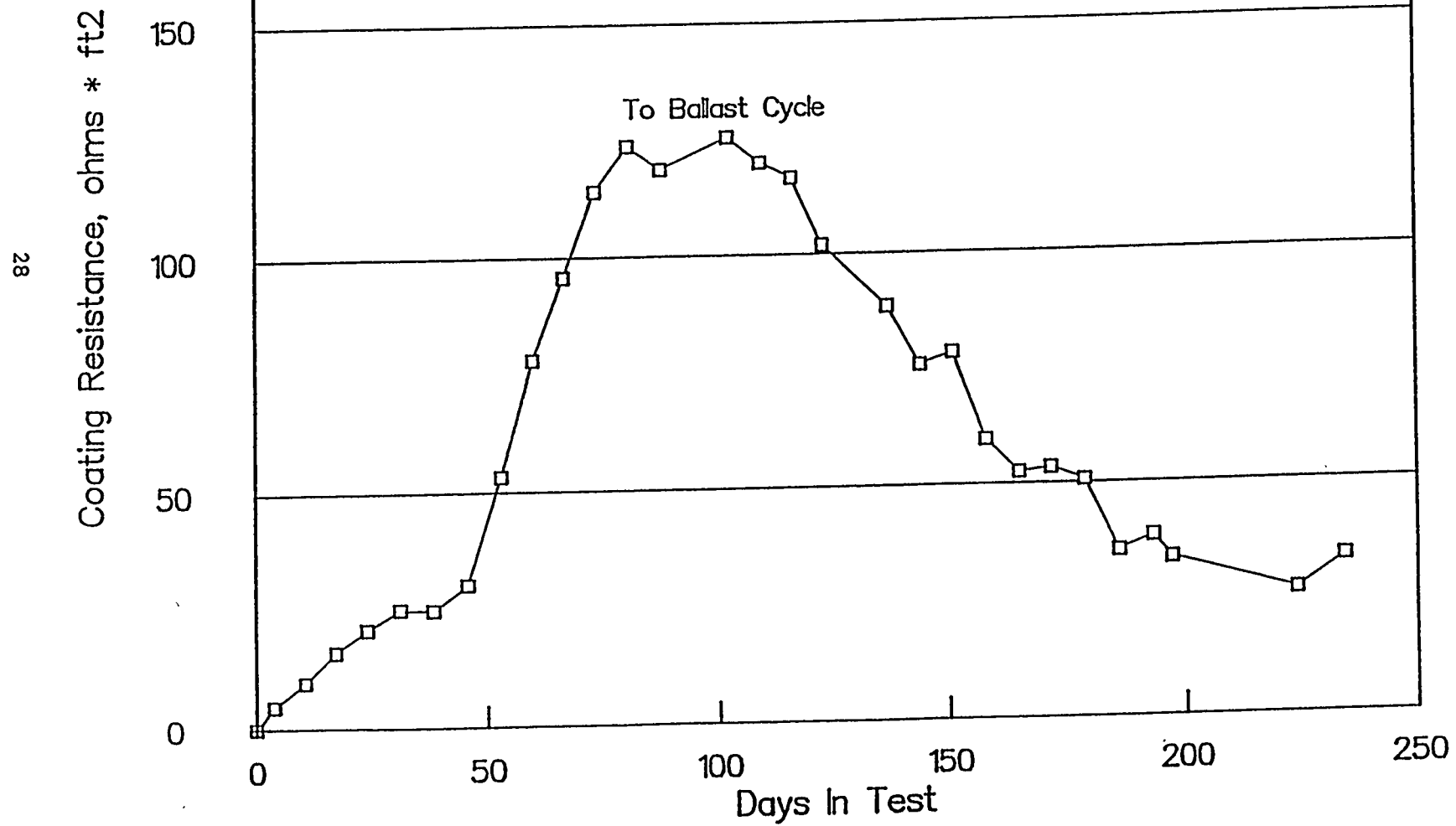


Figure 15 - Coating Resistance vs. Time, Air Agitated Calcite

Calcareous Deposits Over Inorganic Zinc Preconstruction Primer

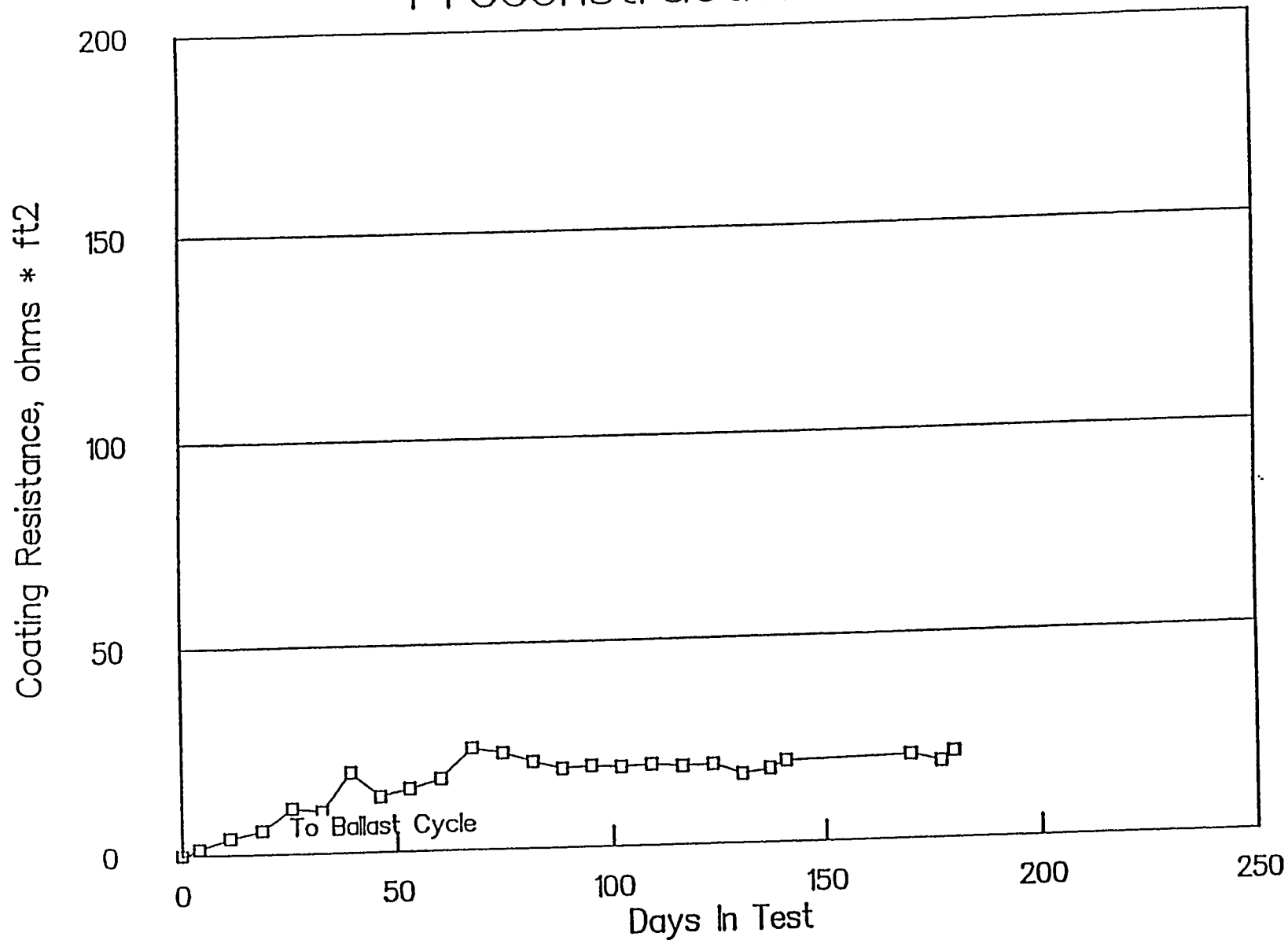


Figure 16 - Coating Resistance vs. Time, Calcareous Deposits over Zinc

Calcite Coating Over Inorganic Zinc Preconstruction Primer

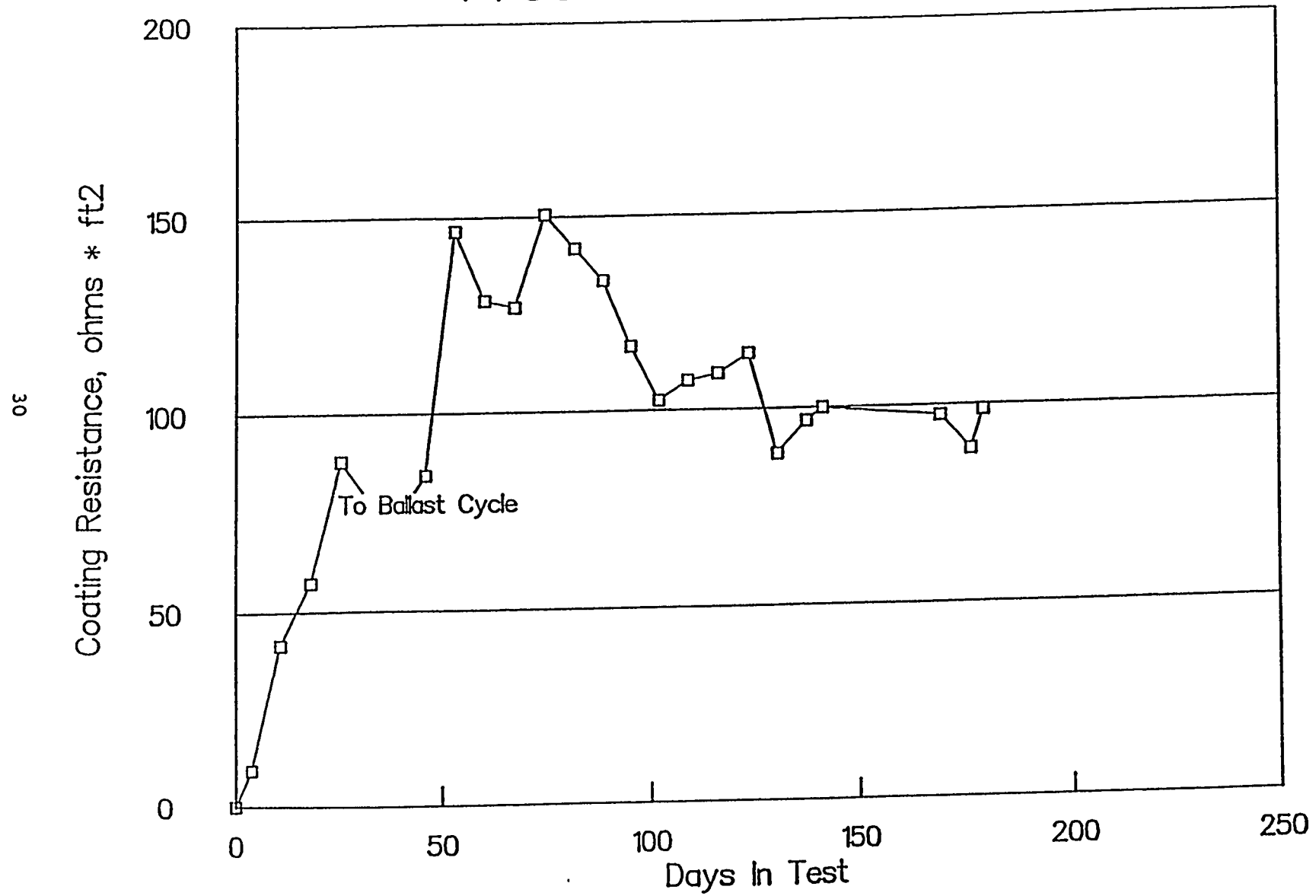


Figure 17 - Coating Resistance vs. Time, Calcite over Zinc

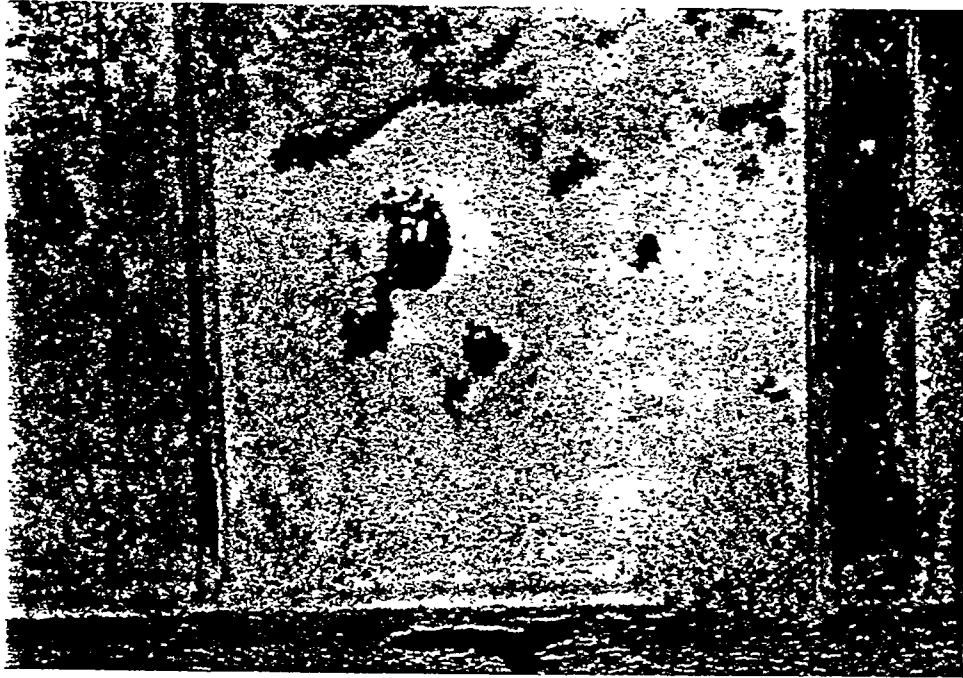


Figure 18 - Steel Tank Originally Coated with
Calcareous Deposit After 100-Day
Seawater Ballast Cycle

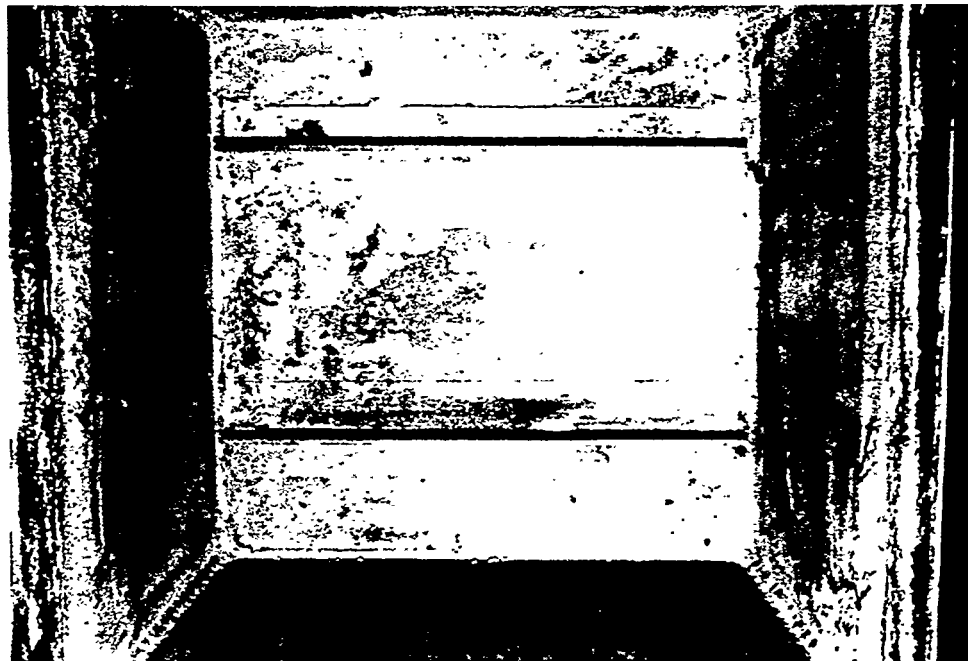


Figure 19 - Steel Tank Originally Coated with
Calcite Coating (Stirred Solution,
40 Days) After 100-Day Seawater
Ballast Cycle

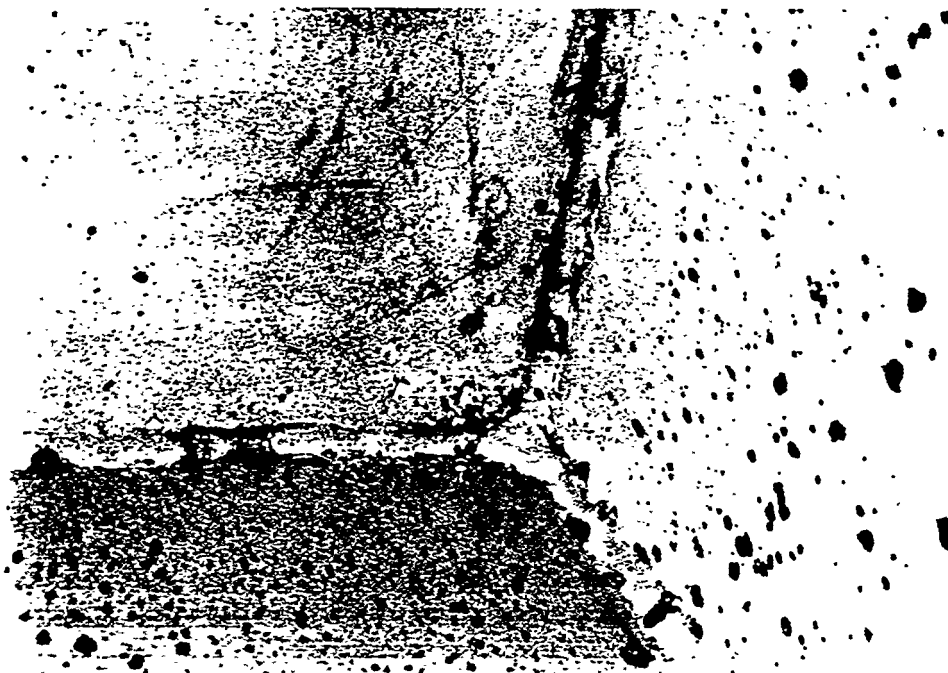


Figure Steel Tank Originally Coated With Calcite
Coating (Water Circulation, 40 Days) After
195-Day Seawater Ballast Cycle

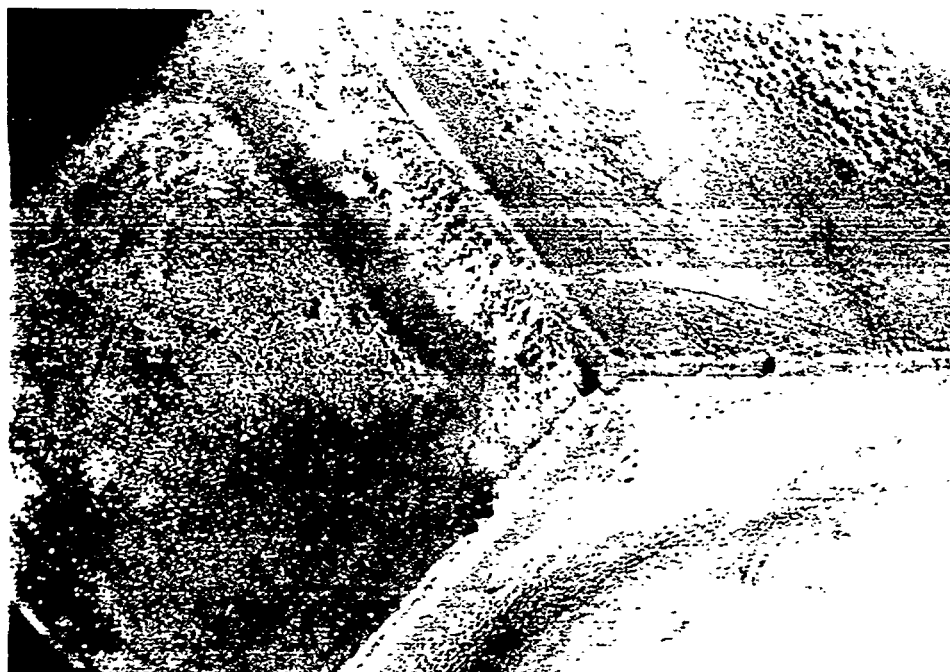


Figure 21 - Steel Tank Originally Coated with Calcite
Coating (Air Agitation, 80-Days) After
155-Day Seawater Ballast Cycle

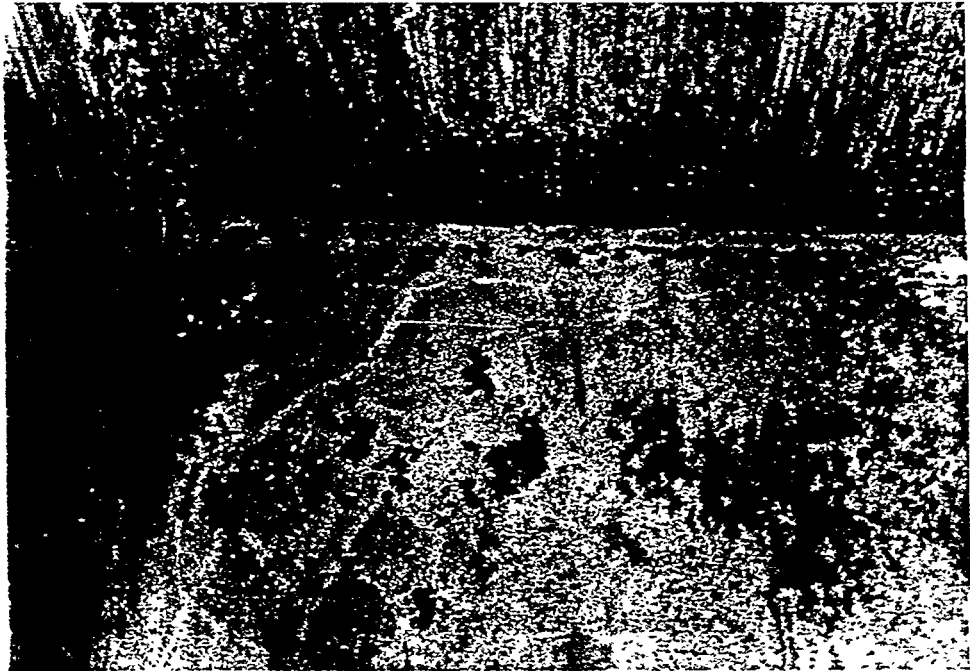


Figure 22 - Steel Tank Originally Primed with Inorganic Zinc and Coated with Calcareous Deposit (Static, 40 Days) After 150-Day Seawater Ballast Cycle



Figure 23 - Steel Tank Originally Primed with Inorganic Zinc and Coated with Calcite (Static, 40 Days) after 150-Day Seawater Ballast Cycle

Current Flow vs. Time

34

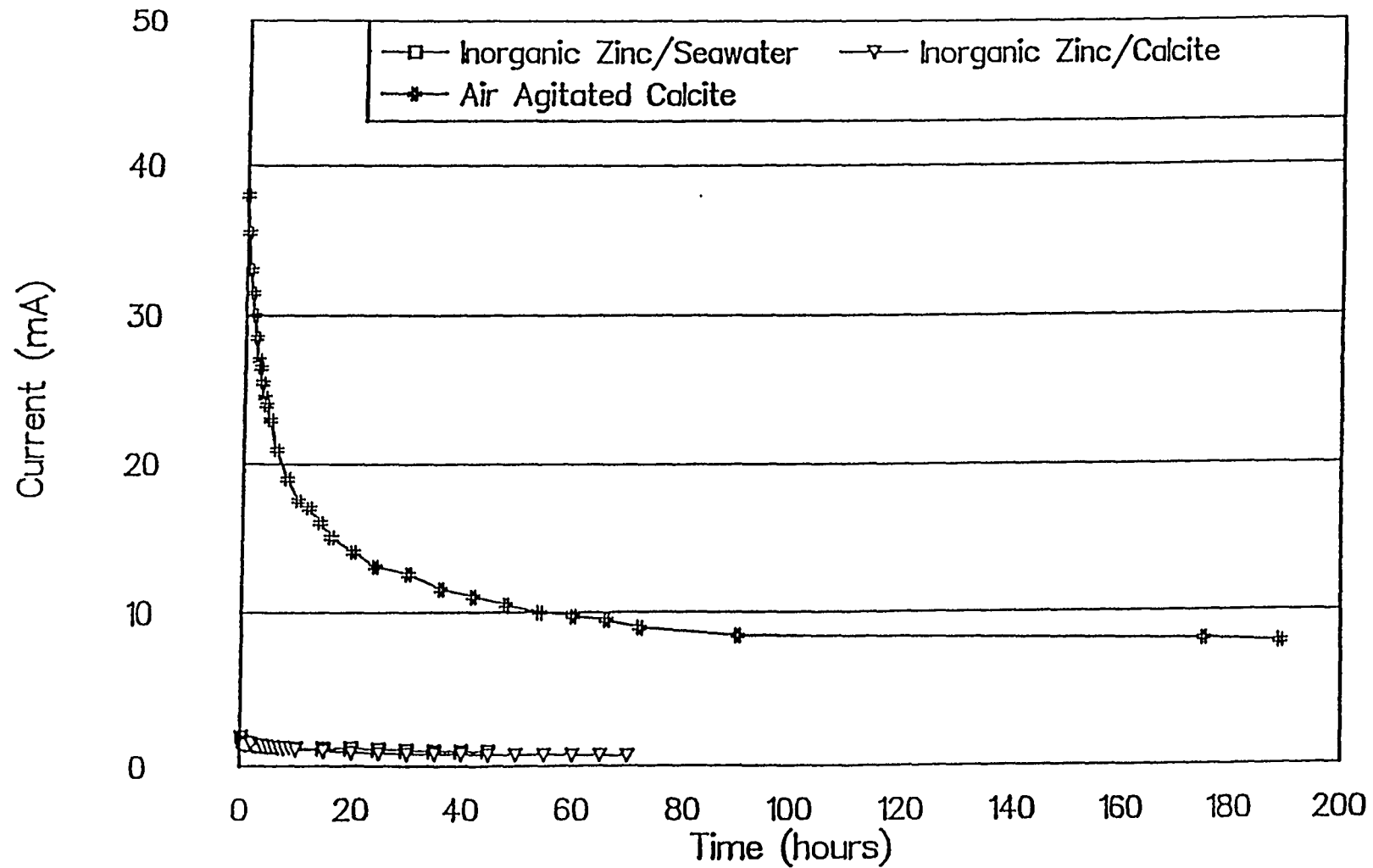


Figure 24 - Current Flow vs. Time for Ballast Tanks